In RbCl:Ag^+ and RbBr:Ag^+ the off-center wells are shallower and no freezing point was observed down to 23°K. As in KCl:Cu^+ the stress effects of the band intensity are proportional to 1/T and come up to $(f_n - f_\perp)/f$ = 0.2 in RbBr:Ag^+ at 100 kp/cm^2. This temperature dependence indicates the same stress-induced mechanism we found for KCl:Cu^+, but off-center positions in [011]-directions give the only possible arrangement which is consistent with our measurements. Since Kapphan and Lüty (3) found no electro-caloric effect in RbBr:Ag^+ at 5°K, we conclude that the freezing point of the Ag^+ ion in RbBr lies between 5°K and 23°K. We point out that [011]-off-center positions in contrast to [111] positions indicate a ds hybridisation of axial symmetry for the ground state of the Ag^+ defect ion.

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OPTICAL PHONONS AND PHASE TRANSITIONS IN SOME ORDER-DISORDER AND DISPLACIVE FERROELECTRICS*

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I - INTRODUCTION

The optical vibrational modes of SbSI and KH_2PO_4 and its isomorphous crystals have received considerable investigation in the past using optical techniques (1)-(3). However, assignment of the modes to the irreducible representations of the proposed space groups in both the paraelectric and the ferroelectric phases has not been complete and the mechanism of the phase transition has not been fully understood in all these crystals. In the present work the polarized Raman spectra of SbSI and KH_2PO_4, $KD_{2x}H_{2(1-x)}PO_4$ (x = .3, .8, .98), KH_2AsO_4 and $NH_4H_2PO_4$ have been measured as a function of temperature in the range 15-300°K.

Complementary polarized far infrared reflectance spectra of all the materials have been measured over the same temperature range. In the present work we have obtained the frequencies and symmetries of the phonon modes as allowed by group theory, and provided confirmation of the proposed structures. The data indicate that the low frequency phonons are 'soft' modes and are responsible for the ferroelectric behaviour. The results confirm current theories concerning the different mechanism of the phase change in ferroelectrics.

II - EXPERIMENTAL

The polarized far infrared reflectance measurements were made using a Fourier transform Michelson interferometer and a low temperature detector. A mosaic was constructed from the SbSI single crystal needles mounted with their c axes parallel to provide about 5 mm x 10 mm surface area. The KDP type crystals were in the form of large polished plates with the c axis parallel to one face.

The Raman spectra were recorded using a Spex 1401 double monochromator, ITT FW130 photomultiplier tube and photoelectron counting detection electronics. A ~ 80 mw 6328Å He-Ne laser with oblique angle scattering was used for SbSI and a ~ 300 mw 5145Å Ar^+ laser with a right angle scattering was used for the KDP type crystals.

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